



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 10 LABORATORY
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**QUALITY ASSURANCE MEMORANDUM
FOR INORGANIC CHEMICAL ANALYSES**

DATE: July 7, 2017

TO: Brenda Bachman, Project Manager
Office of Environmental Review and Assessment, US EPA Region 10

From: Theresa McBride, Chemist
Office of Environmental Review and Assessment, US EPA Region 10 Laboratory

SUBJECT: Quality Assurance Review of the Discovery Bay Seafarms Project
For Metals by ICP-AES

Project Code: WTR-187A
Account Code: 20172018B10P202BD4X24

CC: Margo Young, Aquatic Resources Unit, OERA, USEPA Region 10
Burt Shephard, Risk Evaluation Unit, OERA, USEPA Region 10

The following is a quality assurance review of the results of the analysis of 12 oyster shell samples (and subsections) for metals. These samples were from among those submitted from the Discovery Bay Seafarms Project. A subset of samples was selected with the input of Burt Shephard, to evaluate the samples with the most pronounced discoloration and/or unusual morphology. The analyses were performed by EPA chemists at the US EPA Region 10 Laboratory in Port Orchard, WA, following US EPA and Laboratory guidelines.

This review was conducted for the following samples:

17120100 (4 month old oyster shells)
17120101 (Newly settled oyster shells)

Adult Oysters:

17120102	17120103	17120105	17120106	17120107	17120109	17120110
17120113	17120114	17120117				

The adult oysters were analyzed in subsections. In most cases, three subsections were analyzed (the exception was sample 17120109 which only had two visibly different shell areas). See the photographs submitted with the project for further information.

Subsection A: The newest growth area around the edge of the shell. Frequently thin and fragile.
Subsection B: The middle growth area. Frequently the most discolored section.
Subsection C: The central part of the shell. Frequently less discolored than subsection B.

Portions of the adult oysters were obtained with the aid of a Dremel tool. A digestion of the Dremel blade is provided as IS061617CBL. See section 6 for further information.

Data Qualifications

Comments below refer to the quality control specifications outlined in the Laboratory's current Quality Assurance Manual, Standard Operating Procedures (SOPs) and the Quality Assurance Project Plan (QAPP). A method excursion was required

due to the levels of calcium present in the samples, which was addressed by correcting results using analytical spike data. The excursion (which was discussed as acceptable methodology for this project in the QAPP) is discussed in the **Interferences** section below.

The quality control measures which did not meet Laboratory/QAPP criteria are annotated in the title of each affected subsection with "Laboratory/QAPP Criteria Not Met". Additional information which may affect data usage is discussed in a "NOTE:" which concludes the affected section.

For those tests for which the USEPA Region 10 Laboratory has been accredited by The NELAC Institute (TNI), all requirements of the current TNI Standard have been met.

1. Sample Transport and Receipt

Upon sample receipt, all conditions met Laboratory/QAPP requirements for this project

2. Sample Holding Times

The concentration of an analyte in a sample or sample extract may increase or decrease over time depending on the nature of the analyte. For this reason, holding time limits are recommended for samples.

Holding times were not applicable for this project. Metals in shells are expected to be stable.

3. Sample Preparation

The juvenile oyster shell samples were rinsed repeatedly with reagent water. The adult oyster shells were washed under reagent water using a nylon-bristle brush to remove dirt and other adhering material. The cleaned oyster shells were dried in a 60 °C oven for at least 24 hours.

The juvenile oyster shells were each analyzed in triplicate.

The adult oyster shells were divided into the subsections described above. The subsection A portion of the shells was fragile and was separated from the rest of the shell using clean forceps. Subsections B and C were excised from the body of the shell using a Dremel tool equipped with a cutting disc.

Samples and subsections of samples were acid digested following EPA Method 3050B according to laboratory SOPs.

No qualification of the data was required based on sample preparation.

4. Initial Calibration and Calibration Verification

The standardizations generated for the initial calibrations met method criteria. The Minimum Reporting Level (MRL) of the method is verified on each day of analysis by including it as the low point on the calibration curve, and/or by measuring it as a QC standard. All calibration verification checks met the frequency and recovery criteria on the day of analysis. No qualification was required based on calibration or calibration verification.

5. Laboratory Control Samples

All laboratory control sample results met the recovery acceptance criteria for the method. No qualification was required based on laboratory control sample analysis.

6. Blank Analysis

The method blanks did not contain detectable levels of analyte which would require data qualification.

NOTE: Sample IS061617CBL was a “blank” that consisted of an entire Dremel blade dissolved according to the digestion method. This was analyzed to determine the contents of the blade, and assess any possible contribution to the samples. The blade came in contact with the shells, and was degraded in the process of cutting the shells, creating dust. This dust was removed as much as possible from the shell fragment prior to digestion, but some residue may have remained. The amount that would have adhered would be orders of magnitude less than the contents of the complete blade. Note also that most of the elements which were detected in the blade were not at detectable levels in the shells.

7. Internal Standards

All internal standards met instrument response criteria.

8. Duplicate/Triplicate Analysis -Laboratory/QAPP Criteria Not Met

Triplicate analysis was performed on the aggregate juvenile shell samples 17120100 and 17120101.

Duplicate analysis was performed on samples 17120107A and 17120107B.

Sample results which were greater than five times the MRL level were within the +/- 20% relative percent difference (RPD) requirement, with the following exceptions:

Iron in sample 17120107A had an RPD of 101%. Iron in the “A” subsection samples were qualified (J), estimated.

Iron and Zinc in sample 17120100 had RPD values outside the criteria limits (native/duplicate and native/triplicate of 42.9%/5.3% for Iron and 78.9%/107.2% for Zinc). Iron and Zinc in samples 17120100, 17120100DU and 17120100TR were qualified (J), estimated.

Barium and Iron in sample 17120101 had RPD values outside the criteria limits (native/duplicate and native/triplicate of 5.3%/22.8% for Barium and -8.1%/63.5% for Iron). Barium and Iron in samples 17120101, 17120101DU and 17120101TR were qualified (J), estimated.

No additional qualification was required based on duplicate analysis

9. Matrix Spike/Matrix Spike Duplicate Analysis -Laboratory/QAPP Criteria Not Met

Matrix spike analyses were performed on samples 17120101 and 17120107B. For results where the spike added was less than one-fourth of the native sample concentration (and thus difficult to effectively evaluate), spike results may be designated “NA” with no numerical value given. Applicable spike results were within the 75-125% recovery requirements, with the following exceptions:

Sodium in sample 17120107BS2 was outside acceptance limits at 131%. All sodium results for “B” and “C” subsection samples were qualified (J), estimated.

Aluminum in sample 17120101S1 was outside acceptance limits at 126%. Aluminum results in samples 17120100, 17120100DU, 17120100TR, 17120101, 17120101DU and 17120101TR were qualified (J), estimated.

Silver in sample 17120107BS1 was outside acceptance limits at 60%. All silver results for “B” and “C” subsection samples were qualified (J), estimated.

No additional qualification was required based on matrix spike analyses.

10. Interferences

Inter-element correction checks were analyzed to demonstrate that interferences were under control. All results of these checks met laboratory acceptance criteria.

Serial dilution checks were performed to assess possible interference due to the high calcium matrix. Al, Ca, Mg, Na, and K were reported from diluted samples in order to meet serial dilution requirement. These elements were generally present at sufficient concentration to still be detectable in diluted samples.

The other elements of interest were not present in sufficient quantity to be detectable in diluted samples. Therefore, each undiluted sample was analyzed along with two separate analytical spikes. The analytical spikes indicated the degree to which the calcium matrix was affecting the analyte measurement. The recoveries of the two analytical spikes for each element were averaged, and the result was used to correct the corresponding analyte result.

11. Reporting Limits

All sample results that fall below the MRL are assigned the value of the MRL and the 'U' qualifier is attached. MRL values for some analytes have been elevated to reflect dilutions which were performed to mitigate interferences, or to bring analyte concentrations within the method calibration range.

NOTE: MRL levels are also impacted by the amount of sample digested; consequently, samples with low mass (subsection "A" samples in particular) may have higher reporting limits than other samples.

Sample results above the MRL but below the LRS are reported to two significant figures; results above the LRS level are reported to three significant figures.

12. Data Qualifiers

The (U) qualifier was attached to all sample results that fall below the MRL.

The (J) qualifier was attached to the Iron results in samples 17120102A, 17120103A, 17120105A, 17120106A, 17120107A, 17120107ADU, 17120109A, 17120110A, 17120113A, 17120114A and 17120117A due to poor duplication.

The (J) qualifier was attached to the Iron and Zinc results in samples 17120100, 17120100DU and 17120100TR due to poor duplication.

The (J) qualifier was attached to the Barium and Iron results in samples 17120101, 17120101DU and 17120101TR due to poor duplication.

The (J) qualifier was attached to the Sodium results in samples 17120102B, 17120103B, 17120105B, 17120106B, 17120107B, 17120107BDU, 17120109B, 17120110B, 17120113B, 17120114B, 17120117B, 17120102C, 17120103C, 17120105C, 17120106C, 17120107C, 17120109C, 17120110C, 17120113C, 17120114C and 17120117C due to a high matrix spike recovery.

The (J) qualifier was attached to the Silver results in samples 17120102B, 17120103B, 17120105B, 17120106B, 17120107B, 17120107BDU, 17120109B, 17120110B, 17120113B, 17120114B, 17120117B, 17120102C, 17120103C, 17120105C, 17120106C, 17120107C, 17120109C, 17120110C, 17120113C, 17120114C and 17120117C due to a low matrix spike recovery.

The (J) qualifier was attached to the Aluminum results in samples 17120100, 17120100DU, 17120100TR, 17120101, 17120101DU and 17120101TR due to a high matrix spike recovery.

Below are the definitions for the codes used qualifying data from these analyses. When more than one quality issue was involved, the most restrictive qualifier has been attached to the data. (REMOVE ALL THAT DO NOT APPLY.)

U - The analyte was not detected at or above the reported value.

J - The identification of the analyte is acceptable; however the reported value is an estimate.

UJ - The analyte was not detected at or above the reported value. The reported value is an estimate.

The usefulness of qualified data should be treated according to the severity of the qualifier in light of the project's data quality objectives. Should questions arise regarding the data, contact Katie Adams at the Region 10 Laboratory, phone number (360) 871-8748.

13. Definitions

Accuracy - the degree of conformity of a measured or calculated quantity to its actual value.

Duplicate Analysis – when a duplicate of a sample (DU), a matrix spike (MSD), or a laboratory control sample (LCSD) is analyzed, it is possible to use the comparison of the results in terms of relative percent difference (RPD) to calculate precision.

Internal standards – Compounds used to help evaluate instrument analytical performance for individual samples. Internal standards provide an instrument response for reference to accurately quantify the analytes for all associated instrumental analyses.

Laboratory Control Sample (LCS) – a clean matrix spiked with known quantities of analytes. The LCS is processed with samples through every step of preparation and analysis. Measuring percent recovery of each analyte in the LCS provides a measurement of accuracy for the analyte in the project samples. A laboratory control sample is prepared and analyzed at a frequency no less than one for every 20 project samples.

Low Range Standard (LRS) – A level (often 5 times the MRL) where it has been demonstrated that the instrument achieves defined levels of accuracy and precision (more stringent than at the MRL), as checked with the Low Range Standard during analysis.

Matrix Spike/Matrix Spike Duplicate (MS/MSD) – Sample analyses performed to provide information about the effect of the sample matrix on analyte recovery and measurement within the project samples. To create the MS/MSD, a project sample is spiked with known quantities of analytes and the percent recoveries of the analytes are determined.

Method Blank – An analytical control that is carried through the entire analytical procedure. The method blank is used to define the level of laboratory background and reagent contamination. A method blank is prepared and analyzed for every batch of samples at a minimum frequency of one per every 20 samples. To produce unqualified data, the result of the method blank analysis is required to be less than the MRL and less than 10 times the amount of analyte found in any project sample.

Minimum Reporting Level (MRL) – the smallest measured concentration of a substance that can be reliably measured using a given analytical method.

Precision – the degree of mutual agreement or repeatability among a series of individual results.

Relative Percent Difference – The difference between two sample results divided by their mean and expressed as a percentage.